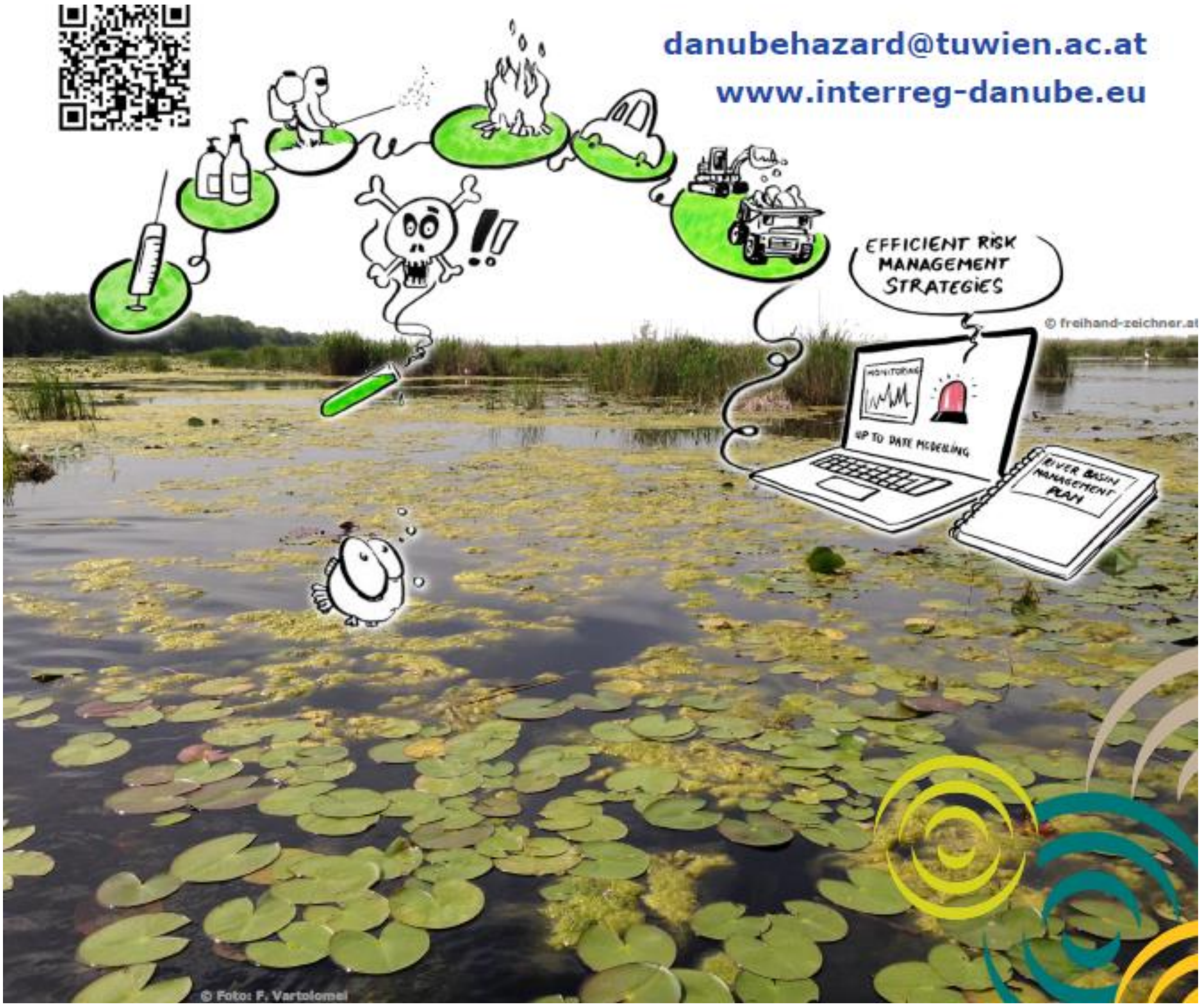
Interreg
Danube Transnational Programme
Danube Hazard m3c

Project Danube Hazard m3c:
Transnational trainings on modelling and scenario evaluation



Output T2.3

Demonstration of the management plan development process at watershed levels for hazardous substances pollution based on detailed emission modelling in seven pilot regions 2023

Factsheet for the Viseu Pilot area

Project co-funded by European Union funds (ERDF, IPA, ENI) and National Funds of the participating countries

PROJECT TITLE: Tackling hazardous substances pollution in the Danube River Basin by Measuring, Modelling-based Management and Capacity building

ACRONYM: Danube Hazard m^{3}c

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1. General introduction

Based on a one-year surface water monitoring, samples were taken once a week and combined to two-months composite samples and analyzed. Sampling took place mostly at low and mean flow conditions. The monitoring was established in all seven pilot regions over four countries (RO, BG, HU, AT) with 20 surface water monitoring sites. From these results a mean annual concentration was calculated, which should be comparable to 12 fold monthly monitoring results, often used for the risk assessment under the Water Framework Directive. The risk assessment considers the following different inorganic and organic substances:

- Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA) (industrial chemicals)
- 16 EPA Polycyclic aromatic hydrocarbons (PAHs, industrial chemicals, and combustion by-products)
- Mercury (Hg), Cadmium (Cd), Copper (Cu), Nickel (Ni), Lead (Pb), Zinc (Zn), Chromium (Cr) and Arsenic (As) (metals)
- Diclofenac and Carbamazepine (pharmaceuticals)
- 4-tert-Octylphenol (industrial chemical)
- Nonylphenol (industrial chemical)
- Bisphenol A (industrial chemical)
- S-Metolachlor (herbicide) including Metolachlor-ESA and Metolachlor-OA (metabolites)
- Tebuconazole (fungicide)

Monitoring results from all monitoring stations were compared with the environmental quality standards (EQS) of Directive2008/105/EU (Priority Substances) and with the substances enacted at the national level (National Substance List). Exceedances are shown in Table 1.

Table 1 Number of the exceedance of the EQS in all pilot areas for each substance group

Substance > EQS	Substance Group	No of monitoring sites	No of pilot regions	No of countries	Regulation
PFOS	Industry	9	5	4	Directive 2008/105/EU
Cu	Heavy Metals	2	1	1	National Substance List
Cd	Heavy Metals	2	1	1	Directive 2008/105/EU
Zn	Heavy Metals	2	1	1	National Substance List
s-Metolachlor	Pesticides	2	1	1	National Substance List

In a second step, for each substance with risk, dominant pathways were evaluated for each catchment by means of emission modelling. Considering the dominant polluters or pathways, scenarios were formulated, which, in a first step address and outline the general potential of a specific measure to mitigate pollution.

The emission modelling was carried out for 34 sub-catchments in seven pilot areas which are situated in four countries. A detailed description of the model, the modelling results and validation can be found in OT 2.2 Report on improved system understanding.

> **Note:** The new proposals of the revised Priority Substance List were also assessed, but do not form a legal basis for the designation of measures at the present time.

2. General information Viseu Catchment

This paragraph briefly describes the Viseu catchment.

The Viseu catchment devides into three sub-catchments. At the outlet of the modelled section (32001) and for the Tisla tributary (32003), which is influenced by mining, monitoring data are available.

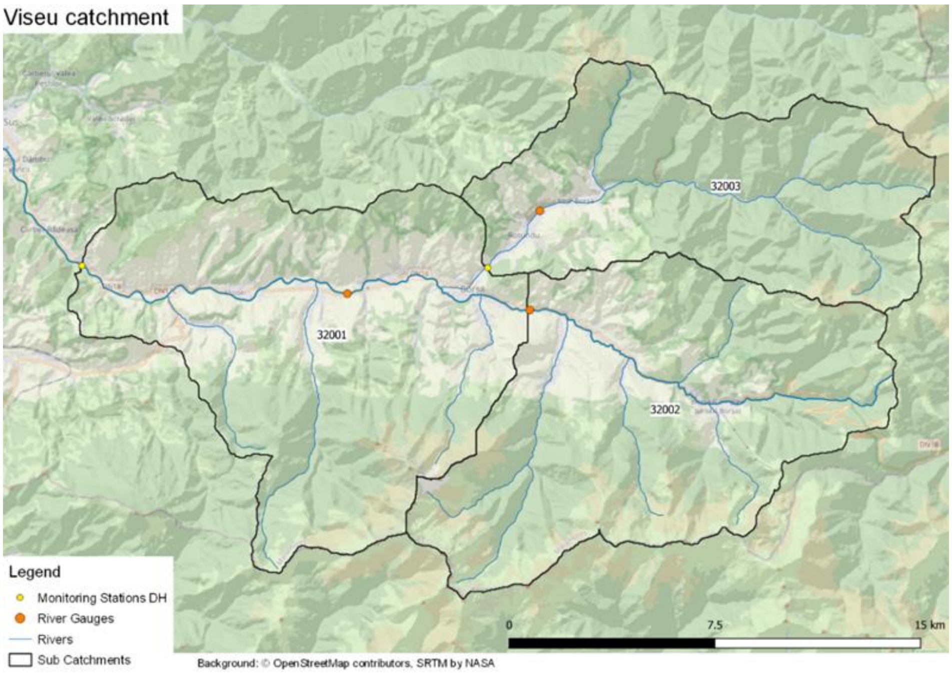


Figure 1 Overview of the pilot area, the sub-catchments and monitoring stations

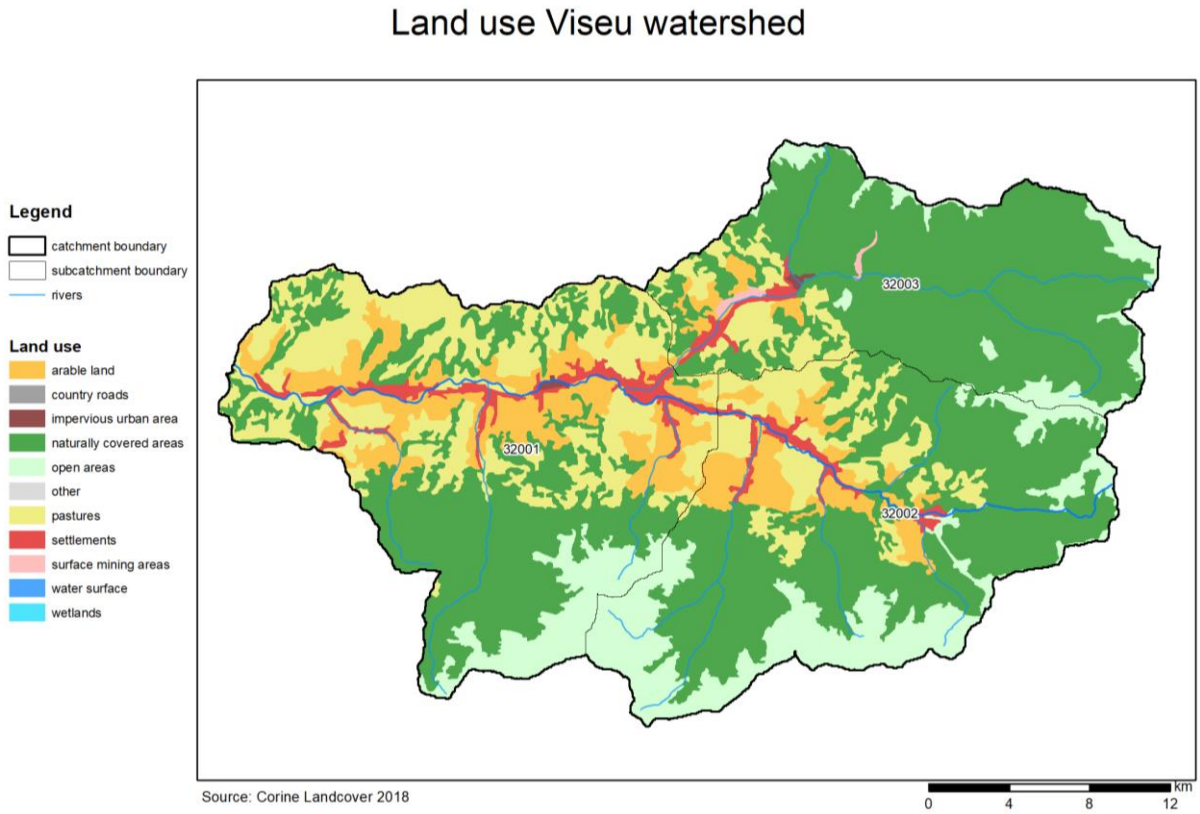


Figure 2 Land use in the pilot area

Forests dominate the upstream regions of the Viseu catchments, which has a mean elevation of more than 1100 m. Pastures are relevant landscape elements. The population density is above the Romanian average and amounts to around 79 inhabitants per km^2. The runoff is the highest of all seven pilot regions under evaluation.

Table 2 Basic information for the Viseu pilot area

Pilot region	Catchment Area [km2]	Mean Eleva-tion [m]	Population density [Inh/km2]	Arable land [%]	Arable land > 4% slope [%]	Pasture [%]	Forest [%]	Urban Area [%]	Runoff [mm]
Viseu	378	1148,3	137	0,2	0,2	20,0	64,8	3,2	959

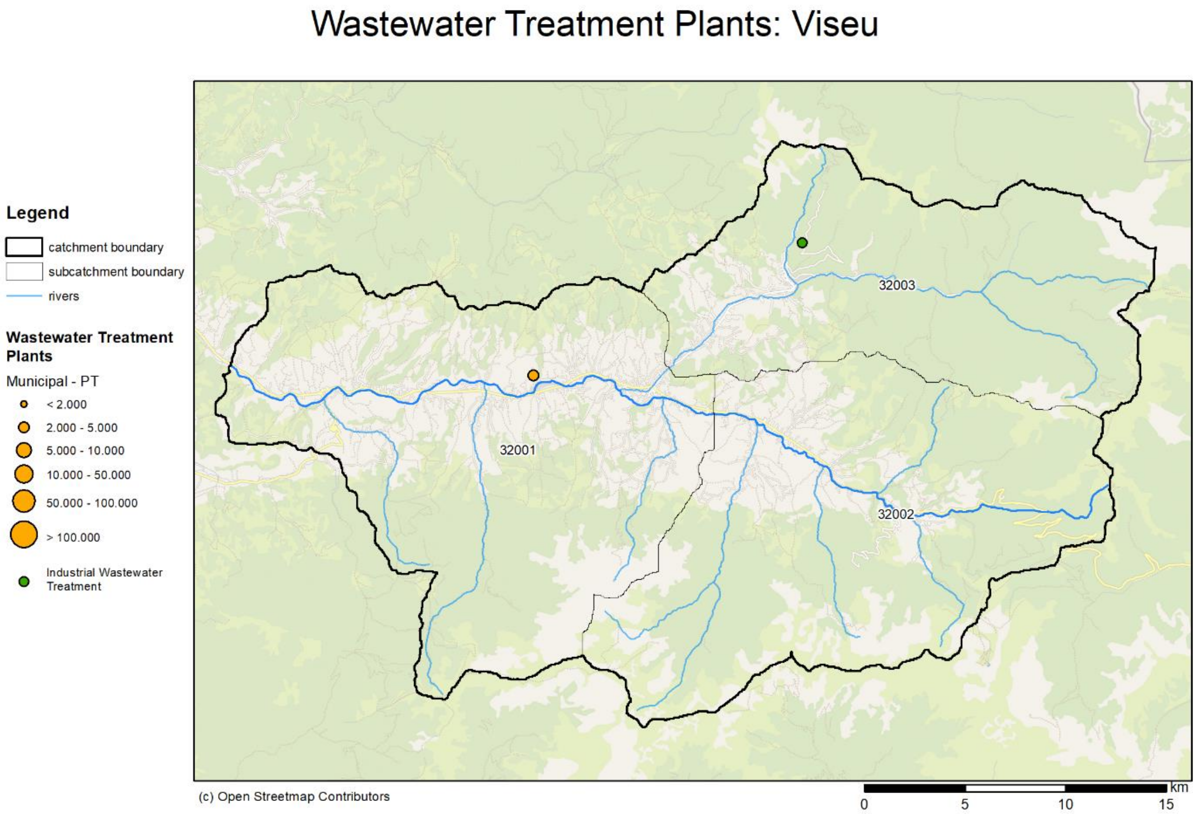


Figure 3 Overview of the point sources in the pilot area

In the Viseu catchment there is one wastewater treatment plan (WWTP) situated in the downstream catchment (32001, treating 2000-5000 PE or inhabitants) and one industrial direct discharger, where surface water from the abandoned mining is treated.

3. Risk assessment: dissolved heavy metals (Cadmium, Copper, Zinc)

The modelled (or measured?) values of Cadmium, Copper and Zinc in sub-catchment 32001 (outlet) and 32003 (abandoned mining influenced area) exceed the EQS by a factor of 3-22 for Cd, 2-4 for Cu and 2-22 for Zn. Modelling results proof that also the sub-catchment 32002 exceeds those EQS, mainly induced by increased groundwater and surface runoff concentrations.

3.1 Specific situation

As mentioned above, the catchment under investigation is heavily influenced by former mining activities. In soil samples, partly high concentrations were found with respect to Cadmium, Zinc and Copper. Concentrations of industrial wastewater treatment plant effluents were high, when influenced by mining (32003), with concentrations of Cu and Zn of 1 and 0,5 mg/l, respectively, and Cd of 0,04 mg/l. Untreated water from five different well known mining effluents, yielded concentrations range in a magnitude of 0,6-4 mg/l for Cu and 2 to 35 mg/l for Zn, while Cd concentration were determined in a range of 0,01 to 0,1 mg/l. One serious problem was the estimation of a valid mean discharge from abandoned mining sites. Rough estimates led to an assumption of 0,054 m^3/s from all five effluents together, which is slightly higher, than the treated effluent from one mining site (0,037 m^3/s).

It should be noted that these estimations and the model results prepared so far underlie significant uncertainties! Nevertheless, using literature data of maximum groundwater concentrations from mining influenced areas, calculations still lead to significant underestimations of dissolved concentrations of Cd, Cu and Zn monitored in the surface water in sub-catchment 32003. This leads to the assumption, that either the discharge of untreated mining water is underestimated or that serious amounts of Cd, Cu and Zn are emitted from unknown, diffuse discharges of abandoned mining sides, from pits, pump sumps, etc. entering the surface water system by percolation, interflow and via small temporary trickles. A combination of both effects is also possible.

Despite these serious uncertainties, it becomes clear that the influence of abandoned mining is a significant threat to surface waters in the Viseu pilot region. At least 60% of the emission of Cu and Zn and 40% of Cd stem from untreated, but well known discharges of abandoned mining in sub-catchment 32003. For Cu, even the discharge of the treated wastewater influenced by mining has a share of the total emission of more than 20%.

In 32002 and 32001 the dominant pathways of dissolved heavy metals are groundwater and with minor influence surface runoff.

Figure 4 shows the area specific modelled dissolved cadmium emissions for all three sub-catchments. For dissolved Cadmium, the area specific emissions in 32002 and 32003 are in the same range, which is explained by the large share of groundwater emissions in 32002 (99%). Details are given in Figure 4.

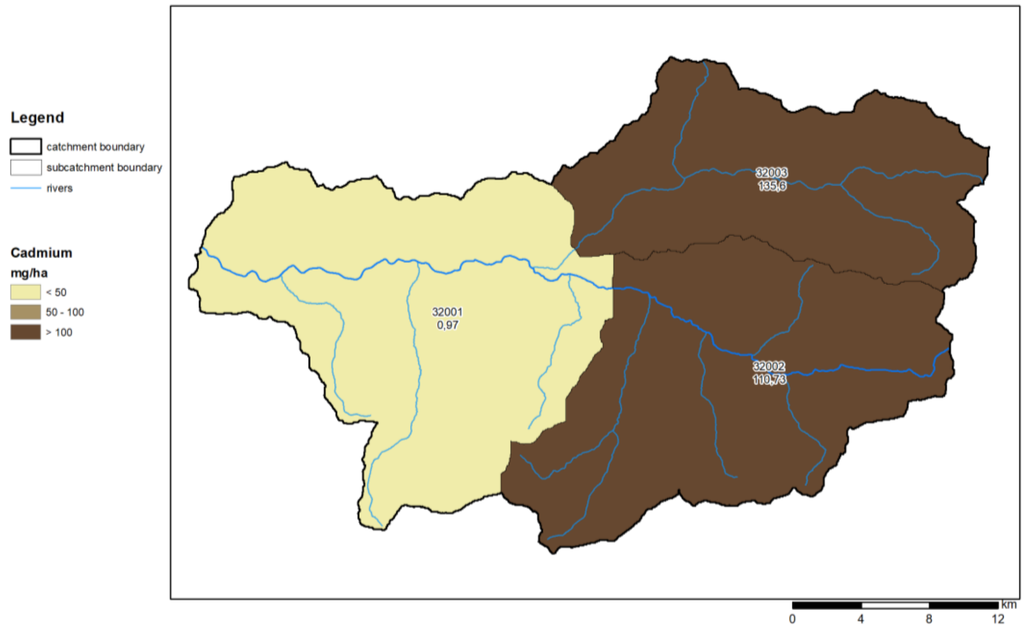


Figure 4 Modelled dissolved Cadmium emission in mg/ha for the Viseu Catchment

Figure 5 shows the area specific modelled dissolved copper emissions for all three sub-catchments. The largest share comes from 32003 with 2756 mg/ha and can be attributed to abandoned mining in 32003. Total emissions from 32002 amount to 643 mg/ha Cu and from 32001 to 141 mg/ha..

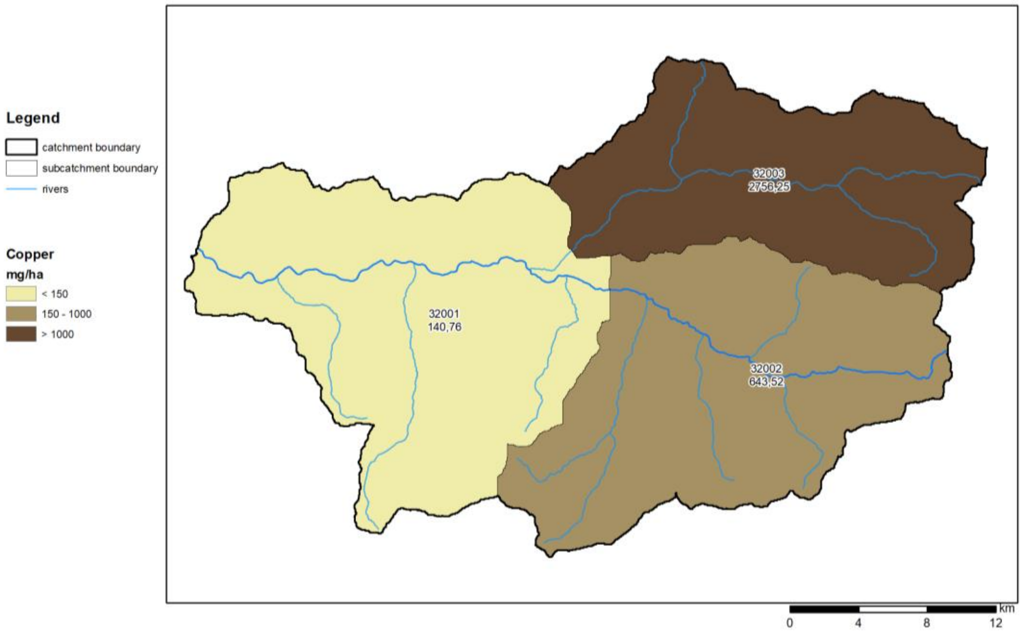


Figure 5 Modelled dissolved Copper emission in mg/ha for the Viseu Catchment

The zinc emissions show a very similar pattern to the copper emissions, both in the area specific total emissions as in the relative shares of the different pathways in the sub-catchments.

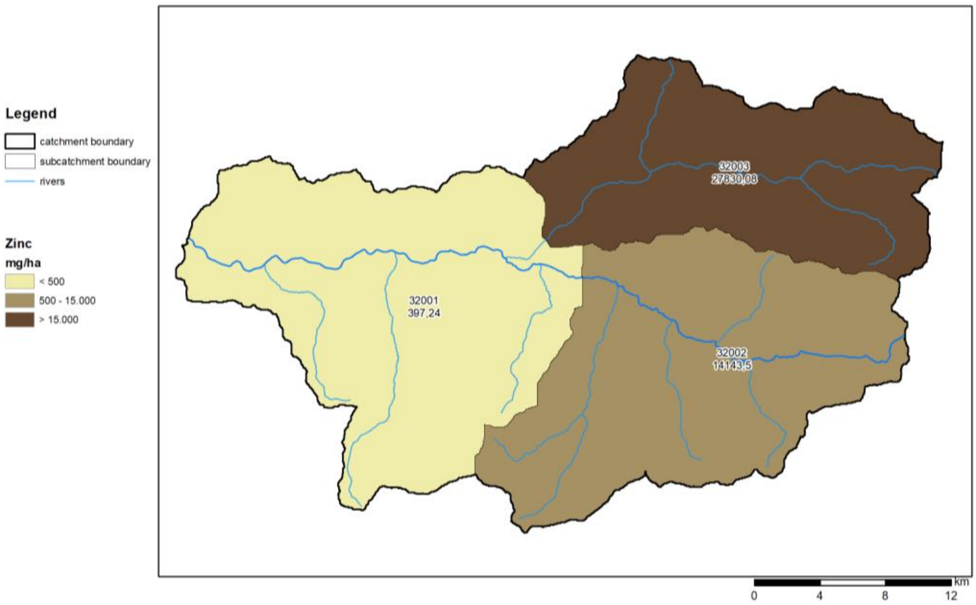
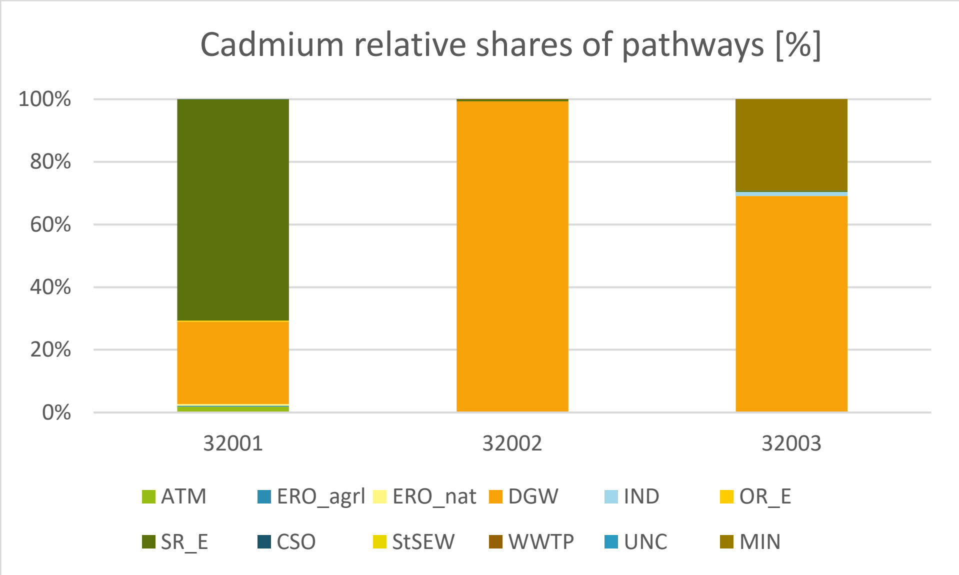
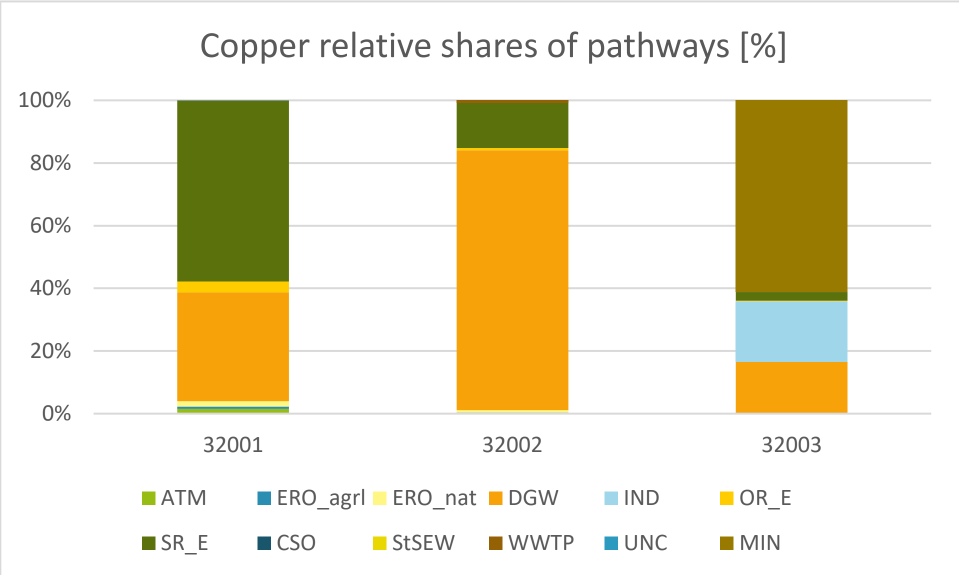


Figure 6 Modelled dissolved Zinc emission in mg/ha for the Viseu Catchment


Cadmium relative shares of pathways [%]
100%
80%
60%
40%
20%
0%
32001
32002
32003
ATM
ERO_agrl
ERO_nat
DGW
IND
OR_E
SR_E
CSO
StSEW
WWTP
UNC
MIN


Copper relative shares of pathways [%]
100%
80%
60%
40%
20%
0%
32001
32002
32003
ATM
ERO_agrl
ERO_nat
DGW
IND
OR_E
SR_E
CSO
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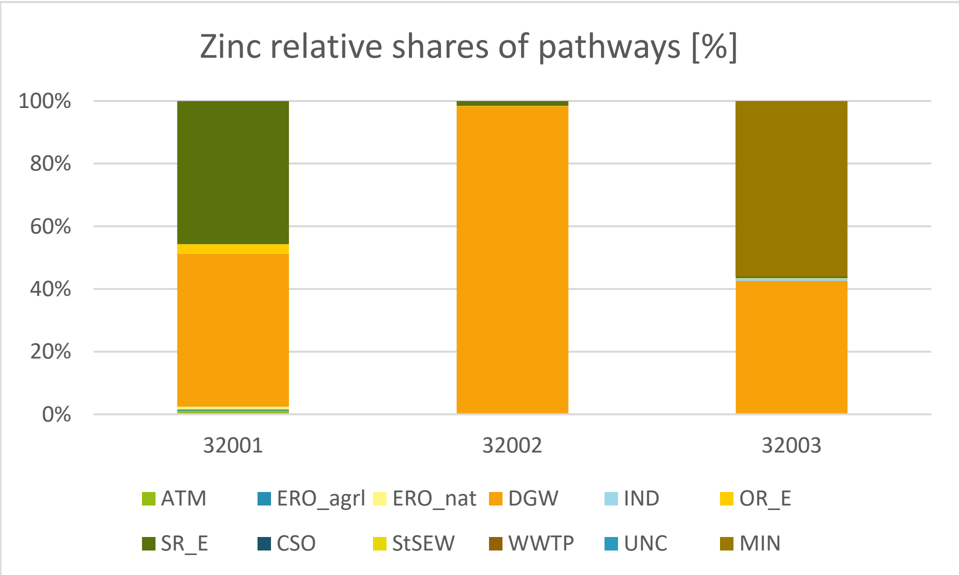
Zinc relative shares of pathways [%]
100%
80%
60%
40%
20%
0%
32001
32002
32003
ATM
ERO_agrl
ERO_nat
DGW
IND
OR_E
SR_E
CSO
StSEW
WWTP
UNC
MIN

Figure 7 relative share of pathways in the Viseu catchment for Cadmium, Copper and Zinc (ATM: atmospheric deposition; ERO_agrl: erosion from agricultural land; ERO_nat: erosion from forests; DGW: groundwater baseflow+interflow+drainages; IND: industrial point sources; OR_E: extra-urban roads; SR_E: surface runoff; CSO: combined stormwater overflow; StSEW: strom sewer; WWTP: municipal WWTP; UNC: sewer systems not connected to WWTP; MIN: abandoned mining)

3.2 Proposals for potential mitigation measures

As a first step the untreated abandoned mining effluent should be treated. f

In treatment plants purification could be managed, resulting in a reduction of the concentrations: 96% (Cd), 90% (Cu) and 86% (Zn) (Diepold, 2020 and Gallagher et al., 2012 With respect to Cu even the existing treatment needs to be significantly improved (which is partly true for Cd and Zn).

The construction of the WWTPs should be planned on base of a detailed register including even suspected contaminated sites and diffuse sources of mining influenced water, percolating to smaller ditches and creeks. Even diffuse runoff from those areas should be collected and treated.

Short – term perspective: Cleaning of abandoned mining water from well-known and diffuse runoff.

Target value: Reduce Cd, Cu and Zn concentrations by 96%, 90% and 86% due to treatment in a WWTP.

Mid-term/Long-term perspective: Groundwater remediation by restoration of most relevant diffuse sources from abandoned mining sites – (prospection, collection and treatment).

Target value: Reduction of groundwater emission by 50%.

3.3 Results from the modeled scenarios

For the Viseu catchment the following scenario was modelled: Treatment of the well known abandoned mining effluent results in a reduction of the concentration of the effluent by 96% for cadmium, 90% copper and 86% for zinc. This measure will result in a reduction of the river concentration of 15-31% for cadmium, 43-57 % for copper and 30-51 % for zinc.

Table 3 Overview of the exceedance of the EQS in all pilot areas

	% reduction in river concentration		
ID of analytical unit	**dissolved Cd**	**dissolved Cu**	**dissolved Zn**
32001	15	43	30
32002	0	0	0
32003	31	57	51

3.4 Initiate stakeholder involvement

In the scope of this project, a questionnaire was set up to collect? information on the feasibility of mitigation measures concerning the reduction of heavy metal concentrations in the Viseu catchment.

The questionnaire for the Viseu catchment was answered by 14 local, regional and national experts. The question if building a WWTP to treat the mining effluent is financially feasible, was answered with yes by 8 experts and with no by 6 experts. The questions about monitoring of the mining effluent and the existence of remediation programs was predominately answered with no (10 out of 14 experts). Also 10 out of 14 experts believe that a modernization of the existing WWTP is feasible. 6 experts think that a reduction of the heavy metals can be established by other measures such as, other greening measures, pretreatment at the source, construction of WWTPs and treatment directly at the source by various methods.

4. Closing data gaps

First and foremost, a detailed investigation of the abandoned mining in the Viseu catchment is needed. At this moment, there is no knowledge of diffuse emissions from the abandoned mining. Furthermore, the runoff of the well-known and monitored abandoned mining effluents should be collected.

For this project for Romania, erosion data from JRC were used. For Romania the erosion rates in both catchments where reasonable, however it is advised that a countrywide erosion model should be developed.

5. Literature:

Diepold, V. (2020): STOFFFLUSSANALYSE ZU SCHWERMETALLEN IM KLÄRSCHLAMM. Masterarbeit, pp.104.

Gallagher, N., Blumenstein, E., Rutkowski, T., DeAngelis, J., Reisman, D. and Progess, Ch. (2012): PASSIVE TREATMENT OF MINING INFLUENCED WASTEWATER WITH BIOCHEMICAL REACTOR TREATMENT AT THE STANDARD MINE SUPERFUND SITE, CRESTED BUTTE, COLORADO. Proceedings America Society of Mining and Reclamation, 2012 pp 137-153. DOI: 10.21000/JASMR12010137